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(12) # EUROPEAN PATENT APPLICATION

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(54) Improvements in and relating to the preparation of shaped crosslinked materials.

(57) A method and apparatus for the formation of shaped crosslinked polyolefinic materials by subjecting a crosslinkable polyolefinic material to a high pressure in a high pressure treatment zone (34), passing the material from said high pressure treatment zone to a relaxation and expansion zone at a temperature below that at which crosslinking takes place, and thereafter shaping and heating the material to a temperature above that ~~at which crosslinking occurs and allowing~~ the crosslinking reaction to proceed substantially to completion.

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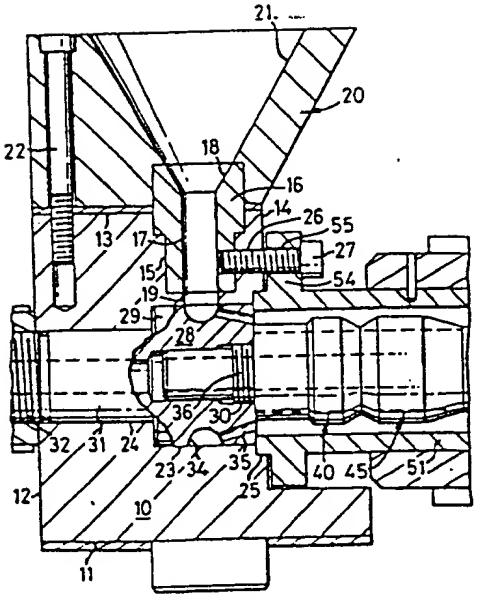
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FIG.3

DESCRIPTION

The present invention relates to the production of shaped crosslinked materials. A satisfactory process for the manufacture of shaped crosslinked materials, particularly shaped crosslinked polyolefinic materials, is described and claimed in British Patent Specification No. 1,158,011. This Specification discloses a process for the manufacture of shaped articles of a crosslinked thermoplastics material which process comprises mixing a thermoplastic material capable of forming a free radical with a cross-linked agent and subjecting the material to instantaneous compression at a pressure in excess of 2000 atmospheres under conditions such that substantial crosslinking of the thermoplastic material does not occur, thereafter forming shapes of the mixture and causing or allowing crosslinking of the shaped material to take place.

In a practical embodiment of the invention forming the subject of Patent No. 1,158,011 the material is extruded and the extrusion is carried out prior to substantial crosslinking of the material taking place.

It will be appreciated that where one is using a crosslinking agent the system is temperature

dependant. The material to be shaped is heated to a temperature below the threshold temperatures at which crosslinking is initiated and the material can be treated as a thermoplastics material, i.e. it may be worked, molded and shaped. Once the material has attained a temperature at or greater than the threshold temperature at which crosslinking takes place, crosslinking proceeds fairly rapidly so that the material thereafter adopts the properties of a thermoset material.

The purpose of the instantaneous compression is to work the material to produce a uniform temperature rise throughout the body of the material. Since themoplastics materials in general are poor heat conductors, mere heating will result in that portion of the material juxtaposed the heat source achieving a temperature approaching or at the threshold temperature at which crosslinking takes place, whereas the centre of the body of the material is not at that temperature with a result that crosslinking in that area does not occur, thus producing non-uniform properties in the final product. By working the material i.e. by subjecting it to compression, the temperature is raised uniformly throughout the body of the material and can be so maintained during further processing. The temperature

control of the material vis a vis the threshold temperature is of considerable importance and hitherto the principle has been to pass the material through a die so that the working of the material by passage of the material through the die results in a sufficient increase in temperature to raise the material above the threshold temperature at which crosslinking takes place.

Crosslinking of the material then commences and as the material passes along the shaping die, the crosslinking reaction proceeding substantially to completion to form, in the case of the specific example of Patent No. 1,158,011 a crosslinked polyethylenic tube.

This process has been commercially successful. Tubing formed of polyethylene or polypropylene in accordance with Patent No. 1,158,011 has found extensive use as tubing, inter alia for hot water and heating systems, and the material has considerable advantages over the traditional materials of copper and stainless steel for such purposes.

In order to have suitable longevity, it is essential that the tubing produced by this process has uniform properties throughout and the wall thickness should be completely free of voids, vacuities and bubbles.

The need to obtain uniformity of cross-linking, uniformity of dimensions and the avoidence of bubbles and voids and the like is self evident. In practice, however, the process of Patent No. 1,158,011 does not provide the means of obtaining such uniformity of properties in production.

According to the present invention there is provided a process for the formation of shaped crosslinked polyolefinic materials which process comprises subjecting a crosslinkable polyolefinic material to high pressure in a high pressure treatment zone, passing said material from said high pressure treatment zone to a relaxation and expansion zone at a temperature below that at which crosslinking takes place, thereafter shaping and heating the material to a temperature above that at which crosslinking occurs and allowing the crosslinking reaction to proceed substantially to completion.

The crosslinkable material may be a polyolefin in admixture with a crosslinking agent therefor; in a specific example the polyolefin may be polyethylene and the crosslinking agent may be dicumyl peroxide.

In a particular embodiment of the present invention the material may be passed from a high pressure treatment zone to a relaxation and expansion

zone through a breaker plate assembly which provides a back pressure for maintaining high pressure within said high pressure zone and at the same time causes or allows working of the material to further increase the temperature of the material passing into said relaxation and expansion zone. The shaping and heating may be effected in a heated die having at least two constrictions towards the feed end thereof under conditions such that the temperature is not increased above the crosslinking threshold temperature until the material is in the vicinity of the second constriction in the die whereby substantial cross-linking occurs downstream of said second constriction.

The die passage may be of generally annular cross-section to produce a tube and the die passage may be provided with means at or towards the outlet thereof for maintaining a back pressure within said die passage. The crosslinkable polyolefinic material may also include a proportion of lubricant and/or stabiliser.

The present invention also includes an extruder for the continuous shaping of a crosslinkable material which extruder comprises means for subjecting a crosslinkable polyolefinic material to high pressure, a relaxation zone to which material passing from said high pressure zone may be

stressed relieved at a temperature below that at which substantial crosslinking of the material takes place and die means defining a shape to be imparted to the material in which the temperature of the material is increased to at least that at which crosslinking occurs.

The relaxation zone may be defined by a breaker plate assembly deboucing into the upper end of a die passage which constitutes a relaxation zone. The heating and the die means may be effected by the application of external heat and/or by the working of material passing one or more constrictions to provide substantially uniform heating of the material to a temperature at or greater than that at which crosslinking occurs thereby initiating cross-linking reaction. The relaxation zone may comprise a conduit means for the admission of a crosslinkable material thereto from said high pressure means, said conduit having a constriction within a passage to cause or allow working of the material as it passes therethrough and heating means for heating the contents of said passage towards the threshold temperature at which crosslinking takes place.

The die means preferably comprises a longitudinal passage defining the shape to be imparted to the material, heating means to heat said passage and said material and constriction means to effect working of the material towards an

inlet end thereof to raise the temperature of the material above the threshold temperature at which crosslinking takes place thereby allowing crosslinking to proceed to completion as the material passes along the die passage.

Means for maintaining back pressure within the die passage may be a constrictor member arranged at the exit end of said die passage to restrict the exit therefrom of the substantially crosslinked material.

The breaker plate assembly may define a plurality of feed orifices upstream of the relaxation zone and communicating with the high pressure means.

The breaker plate assembly preferably comprises a plate having a plurality of circumferentially spaced orifices through which the material passes from the high pressure means to the relaxation zone.

The high pressure means may comprise a zone in which instantaneous compressions are applied to a mixture of material for generating pressure within the material thereby producing a substantially uniform temperature rise. The pressure generated in said zone is preferably at least 1000 atmospheres.

The material to be supplied to the pressure zone is usually in the form of particulate material together with, for example, residual catalyst and solvents.

The material as supplied may contain a high level of oxygen and moisture. By applying the high pressures in accordance with the present application the substances such, for example, as residual solvent, oxygen and moisture are generally removed or expressed from the composition. The continued application of pressure and the further supply of material results in movement of the material within the pressure zone towards the breaker plate assembly whereby the material is worked as it passes the breaker plate which further increases the internal temperature by the internal working and at the same time serves to improve the uniformity of the material and permits residual pockets or pores containing vaporised solvent and the like to be compressed to provide a substantially pore free and bubble free homogeneous mixture. By passing the material into the expansion zone, immediately behind the high pressure zone, the internal working renders the material substantially plastic and susceptible to being extruded or moulded provided that the temperature of the material is retained below that at which commencement of the crosslinking reaction takes place. The compression and subsequent relaxation permits sufficient working of the material to ensure that

the morphous and crystalline particles in the material form part of a homogeneous mixture and that as the material enters the die, the mixture is substantially uniform in both temperature and composition to provide for substantially uniform crosslinking.

The coefficient of friction within the die means may be substantially reduced by friction reducing agents such as lubricants, stabilisers or by the provision of PTFE or plasma coating on the internal surface of the die passages.

Furthermore, it has been found that by adjusting the back pressure to an appropriate level the formation of bubbles and vacuities within the tube so produced is substantially reduced.

Following is a description by way of example only and with reference to the accompanying informal drawings of method of carrying the invention into effect.

Figure 1 is a view partly in section of a die barrel for producing tube in accordance with the present invention.

Figure 2 is a section through a mandrel and breaker plate assembly for use in combination with the die assembly of Figure 1.

Figure 3 illustrates the mounting assembly for the die assembly of Figure 1.

Referring to Figure 3, a support block 10 has a base 11 and a forward face 12, an upper face 13 and a rear face 14. The upper face 13 is bored at 15 to receive a cylinder piece 16 having a substantially vertically disposed through bore 17 constituting the cylinder which is provided with a frustoconical portion 18 at its upper end, the arrangement being such that through bore 17 communicates with a reduced portion of bore 15. Upper face 13 carries hopper 20, the inner frustoconical surface 21 of which is continuous with frustoconical portion 18 of cylinder piece 16. The hopper 20 is secured to upper face 13 of support block 10 by means of bolts 22 and serves to retain cylinder piece 16 in its operative location. The rear face 14 of support block 10 is provided with a substantially central cylindrical bore 23 which is reduced at 24 towards the forward end of block 10. The rearward extremity of bore 23 is expanded at 25. A plurality of circumferentially spaced bolt holes 26 are provided in rearward face 14 each being tapped to receive a securing bolt 27.

The central bore 23 and associated reduced bore portion 24 is adapted to receive a breaker plate assembly 28 which comprises a substantially cylindrical breaker plate 29 having a central bore

30 in the rearward face thereof and having a forward extension 31 reduced in diameter to fit within reduced cylindrical bore portion 24. The forward extremity of forward extension 31 is threaded at 32 for securing breaker plate assembly 28 within the bore 23 of support block 10. Breaker plate 29 is provided in the cylindrical surface thereof with an annular recess 34 having a substantially semi-circular cross section adapted to communicate with the lower extremity of the reduced portion 19 of bore 17 extending from the upper surface 13 of block 10. The recess is provided with a plurality of circumferentially spaced passages 35 extending from annular recess 34 to the rearward face of breaker plate assembly 28 each passage 35 being substantially cylindrical in cross section and being convergently inclined from annular recess 34 towards the axis of breaker plate assembly 28 in a direction towards the rearward face thereof.

The central concentric bore 30 of breaker plate assembly 28 is adapted to receive a threaded spigot 36 which engages with threads on the internal surface of concentric bore 30, said spigot extending forwardly from a mandrel 37, see Figure 1, of die assembly 38. The mandrel 37 of die assembly 38 is substantially cylindrical and extends the longitudinal length of the die assembly per se.

The mandrel is provided with a threaded counter bore at its rearward end and is adapted to receive a constrictor member 39 having a threaded spigot engaging with counter bore in the rearward end of mandrel 37. The mandrel carries towards its forward end a first constriction element 40 juxtaposed the breaker plate assembly 28. The first constriction element 40 comprises a substantially cylindrical sleeve 41 disposed about mandrel 37 having at its rearward end a forward frustoconical surface 42 and intermediate cylindrical portion 43 and a rearward frustoconical portion 44 which together define an expansion on the overall radial extent of mandrel 37. Mandrel 37 also carries second constriction element 45 contiguous element 40, element 45 comprising a forward frustoconical surface 46, intermediate cylindrical surface 47 and a rearward frustoconical surface 48 to define a second expanded portion on mandrel 37, the longitudinal extent of the second constriction element being greater than the longitudinal extent of the forward constriction element.

The mandrel 37 carries towards its rearward end a further small constriction 49 spaced from constrictor 39.

The die assembly 38 is completed by the provision of an external longitudinally extending sleeve or barrel 51 having a substantially cylindrical

inner surface 52 the inner surface 52 of barrel 51 and the external surface of mandrel 37 serving to define die passage 53 for the passage of material therepass during processing.

A die barrel 51 is provided with a plurality of heating elements thereabout (not shown) and mandrel 37 may also be provided with heating means if this is considered to be desirable. The die barrel 51 is provided at its forward end with a radial flange 54 which is provided with a plurality of circumferentially spaced holes 55 adapted to cooperate with bolt holes 26 to receive bolts 27 to secure the die barrel to support block 10.

A plunger having a piston portion is adapted to enter a piston block 16 as a sliding fit within through bore 17, said plunger being propelled by an eccentric press or the like for the purpose of applying a plurality of instantaneous compressions within the bore itself. In operation a cross-linkable material typically polyethylene together with a cross linking agent such as dicumyl peroxide in a proportion of 1.5 to 3% by weight of dicumyl peroxide based on the weight of polyethylene is placed as a finely divided mixture in the hopper 20 and the reciprocation of the plunger forces material into the through bore 17 of cylinder piece 16, the action of the plunger serving to increase the temperature of the material until the material flows

into the annular recess 34 and via breaker plate assembly passages 35 into the die passage 53.

As the material leaves the circumferentially spaced passages 35 in the breaker plate assembly 28, the temperature of the material is at a temperature below the threshold temperature at which crosslinking commences. The passage of the material into the annular space defined by the cylindrical portion 41 of the first constriction 40 serves to impart momentum to the material leaving the breaker plate assembly 28. As the material passes the first constriction defined by a cylindrical surface 43 the reduction in cross section area in the die passage in this area results in the further working of the material, and a further increase in the temperature towards the threshold temperature followed by a relaxation of the material into the area of increased cross section defined by the rearward frustoconical portion 44 of the first constriction 40 and a forward frustoconical portion 46 of the second constriction element 45.

Further movement of the material along the die results in the material passing a second constriction with further working of the material and additional heat being imparted from the mandrel and from the die barrel 51 which together with the

working of the material serves to raise the material to the threshold temperature at which crosslinking of the material is initiated. Relaxation of the material from the second constriction 45 occurs so that the material is passing along the cylindrical portion of mandrel 37 away from the second constriction element 45 before substantial cross-linking of the material takes place.

The material is maintained within the die assembly in a portion of substantially constant cross section area while the cross-linking action proceeds substantially to completion. As the material approaches the rearward end of the die assembly it passes over rearward constriction 49 and is thus squeezed on exit by means of constrictor 39 in order to provide a back pressure within the die passage 53. The back pressure generated by constrictor 39 serves to ensure intimate contact between the material within the die passage and the walls thereof in order to obtain improved heat transfer from the mandrel and the die barrel during the period in which crosslinking takes place.

It has been found that by using the apparatus and method of invention as described above the material within the die is maintained in intimate

contact with the surfaces of the die assembly and substantially uniform crosslinking takes place while the back pressure ensures a substantial reduction in the formation in bubbles and vacuities in the tube produced.

CLAIMS:-

1. A process for the formation of shaped cross-linked polyolefinic materials which process comprises subjecting a crosslinkable polyolefinic material to high pressure in a high pressure treatment zone, passing said material from said high pressure treatment zone to a relaxation and expansion zone at a temperature below that at which crosslinking takes place, thereafter shaping and heating the material to a temperature above that at which crosslinking occurs and allowing the crosslinking reaction to proceed substantially to completion.

2. A process as claimed in claim 1 wherein the crosslinkable material is a mixture of a polyolefin and a crosslinking agent therefor.

3. A process as claimed in claim 2 wherein the polyolefin is polyethylene and the crosslinking agent is dicumyl peroxide.

4. A process as claimed in anyone of the preceding claims wherein the high pressure is in excess of a 1000 atmospheres.

5. A process as claimed in anyone of the preceding claims wherein the high pressure is generated by means of an excentre press.

6. A process as claimed in any preceding claim wherein the material is passed from the high pressure treatment zone to a relaxation and expansion zone through a breaker plate assembly which provides a back pressure for maintaining high pressure within said high pressure zone and at the same time causes or allows working of the material to further increase the temperature of the material passing into said relaxation and expansion zone.

7. A process as claimed in any preceding claim wherein the shaping and heating is effected in a heated die having at least two constrictions towards the feed end thereof under conditions such that the temperature is not increased above the crosslinking threshold temperature until the material is in the vicinity of the second constriction in the die whereby substantial cross-linking occurs downstream of said second constriction.

8. A process as claimed in any preceding claim wherein the die passage may be of generally annular cross-section to produce a tube.

9. A process as claimed in any preceding claim wherein the die passage may be provided with means at or towards the outlet thereof for maintaining a back pressure within said die passage.

10. A process as claimed in any preceding claim wherein the crosslinkable polyolefinic material includes a portion of lubricant and/or stabiliser.

11. An extruder for the continuous shaping of a crosslinkable material which extruder comprises means for subjecting a crosslinkable polyolefinic material to high pressure, a relaxation zone to which material passing from said high pressure zone is stressed relieved at a temperature below that at which substantial crosslinking of the material takes place and die means defining a shape to be imparted to the material in which the temperature of the material is increased to at least that at which cross-linking occurs.

12. An extruder as claimed in claim 11 wherein the die passage has an annular cross-section to produce a tube.

13. An extruder as claimed in claim 11 or claim 12 including means provided towards the outlet of the die for maintaining back pressure within the die passage.

14. An extruder as claimed in anyone of claims 11 to 13 wherein the relaxation zone is defined by a breaker plate assembly debouching into an upper end of the die passage constituting a relaxation zone.

15. An extruder as claimed in anyone of claims 11 to 14 wherein the heating in the die means is effected by the application of external heat and by the working of the material passing one or more constrictions to provide substantially uniform heating of the material to a temperature at or greater than that at which crosslinking occurs thereby initiating the crosslinking reaction.

16. An extruder as claimed in anyone of claims 1 to 15 wherein the relaxation zone comprises a conduit means for the admission of a crosslinkable material thereto from said high pressure means, said conduit having a constriction within a passage to cause or allow working of the

material as it passes therethrough and heating means for heating the contents of said passage towards the threshold temperature at which cross-linking takes place.

17 An extruder as claimed in anyone of claims 1 to 16 wherein the die means comprises a longitudinal passage defining the shape to be imparted to the material, heating means to heat said passage and said material and constriction means to effect working of the material towards an inlet end thereof to raise the temperature of the material above the threshold temperature at which crosslinking takes place thereby allowing crosslinking to proceed to completion as the material passes along said die passage.

18. An extruder as claimed in claim 13 wherein the means for maintaining back pressure within the die passage is a constrictor member arranged at the exit end of said die passage to restrict the exit therefrom of the substantially crosslinked material.

19. An extruder as claimed in claim 14 when the breaker plate assembly defining a plurality of feed orifices upstream of the relaxation zone and communicating with the high

pressure means.

20. An extruder as claimed in claim 19 wherein the breaker plate assembly comprises a plate having a plurality of circumferentially spaced orifices through which the material passes from the high pressure means to the relaxation zone.

21 An extruder as claimed in anyone of claims 11 to 20 wherein the high pressure means comprises a zone in which instantaneous compressions are applied to a mixture of material for generating pressure within the material thereby producing a substantially uniform temperature rise therewithin.

22. An extruder as claimed in claim 21 wherein the pressure generated is at least 1000 atmospheres.

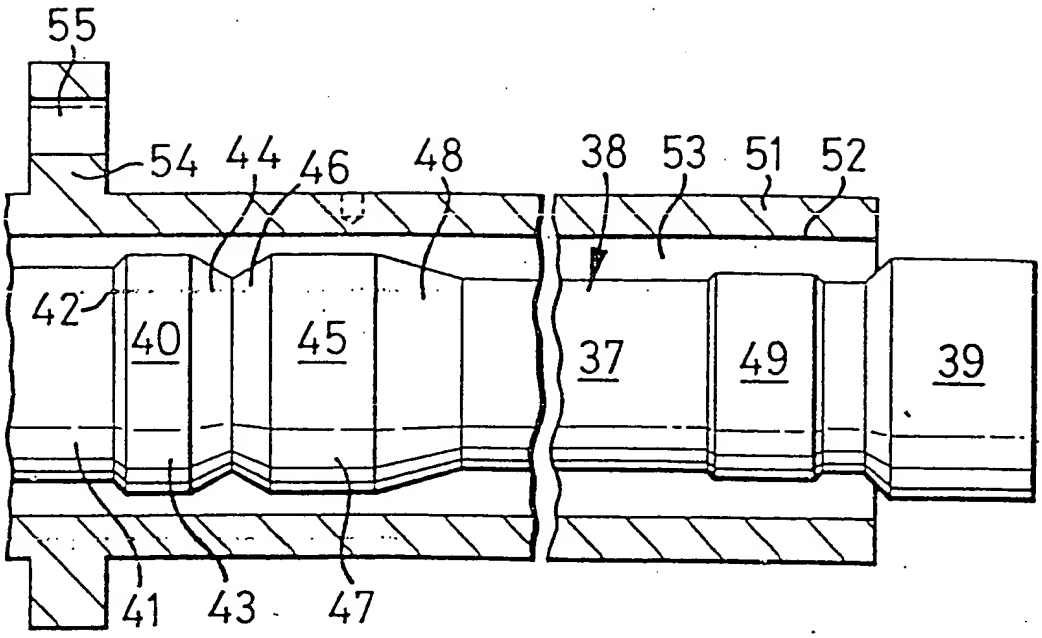
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FIG.1

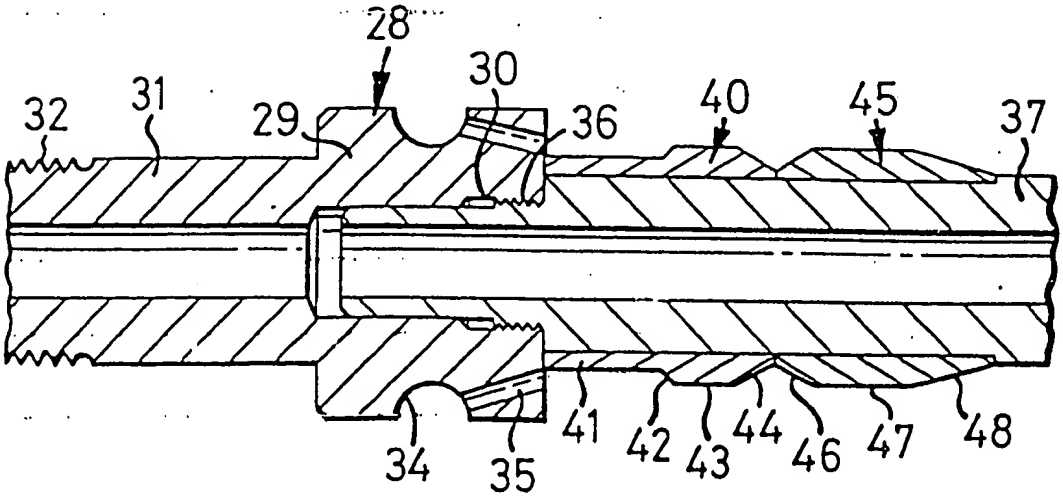
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FIG.2

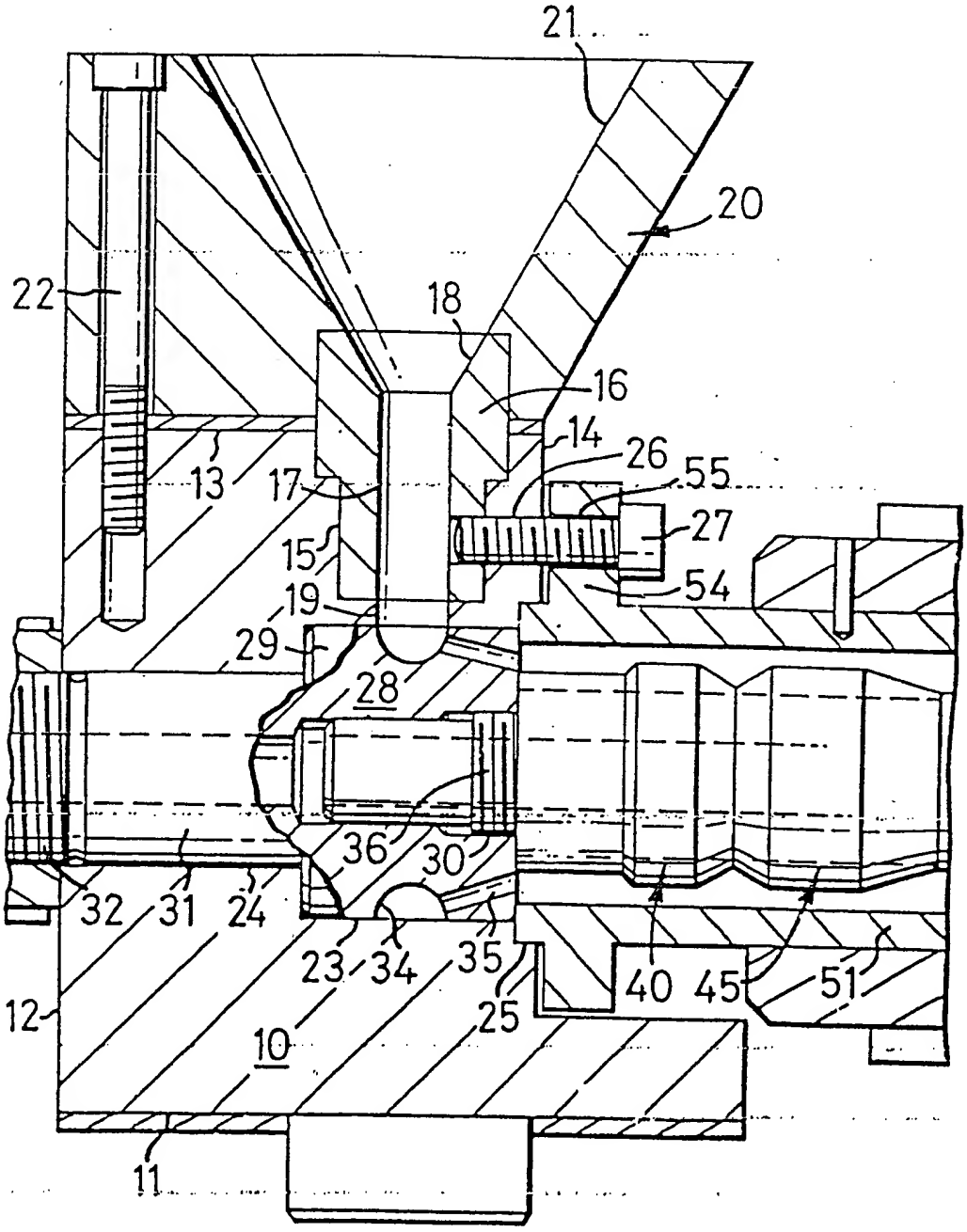
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FIG.3

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# EUROPEAN SEARCH REPORT

Application number
EP 81 30 0125.2

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl.³) |
|---|---|---|---|
| | US - A - 4 089 917 (M. TAKIURA et al.)<br>* claims 1 to 3 * | 1-4,6,<br>7,11,<br>17 | B 29 F 3/00<br>B 29 F 3/06 |
| D | GB - A - 1 158 011 (T.P. ENGEL)<br>* claims 1 to 6 * | 1 | |
| A | US - A - 3 891 372 (M. TAKIURA)<br>* abstract * | | |
| A | US - A- 3 864 069 (M. TAKIURA et al.)<br>* claim 1* | | TECHNICAL FIELDS SEARCHED (Int. Cl.³)<br>B 29 F 3/00<br>B 29 G 2/00<br>B 29 G 3/00<br>C 08 J 3/00<br>C 08 L 23/00<br>H 01 B 3/00<br>H 01 B 13/00 |
| A | US - A - 3 876 736 (M. TAKIURA)<br>* claim 1 * | | |
| A | US - A - 3 985 484 (M. TAKIURA)<br>* claim 1 * | | |
| A | GB - A - 1 292 227 (SÜDDEUTSCHE KA[illegible] WERKE ZWEIGNIEDERLASSUNG DER VEREINIGTE DEUTSCHE METALLWERKE AG)<br>* claim 1 * | | |
| A | DE - A1 - 2 432 758 (BASF AG)<br>* claims 1, 2 * | | |

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CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| Berlin | 10-04-1981 | BITTNER |

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# EUROPEAN SEARCH REPORT

Application number
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| DOCUMENTS CONSIDERED TO BE RELEVANT | | | CLASSIFICATION OF THE APPLICATION (Int. Cl.³) |
|---|---|---|---|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | |
| A | DE - B2 - 1 964 895 (VEREINIGUNG ZUR FÖRDERUNG DES INSTITUTS FÜR KUNSTSTOFFVERARBEITUNG IN INDUSTRIE UND HANDWERK AN DER RHEIN. - WESTF. TECHN. HOCHSCHULE AACHEN) * claim 1 * | | |
| A | GB - A - 1 454 431 (PONT-A-MOUSSON S.A.) * page 2, lines 116 to 126 * | | TECHNICAL FIELDS SEARCHED (Int. Cl.³) |
| A | DD - A - 109 344 (WIRSBO BRUKS AKTIEBOLAG) * claims 1, 2 * | | |
| P | DE - A1 - 2 830 352 (T.P. ENGEL) * claims 1 to 6 * | | |